

## PHYS393 – Statistical Physics

### Part 2: Two Examples of the Boltzmann Distribution

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#### The Boltzmann distribution

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In the previous part of this course, we derived the Boltzmann distribution:

$$n_j = \frac{N}{Z} e^{-\frac{\epsilon_j}{kT}}, \quad (1)$$

where  $n_j$  is the number of particles in the energy state with energy  $\epsilon_j$ ,  $k$  is Boltzmann's constant,  $T$  is the thermodynamic temperature,  $N$  is the total number of particles, and  $Z$  is the partition function:

$$Z = \sum_j e^{-\frac{\epsilon_j}{kT}}. \quad (2)$$

The temperature is a parameter in the distribution, such that the total energy is equal to a specified value,  $U$ :

$$\sum_j n_j \epsilon_j = U. \quad (3)$$

In this part of the lecture course, we shall see what we can learn by applying the Boltzmann distribution to two example systems. These systems are:

- A collection of spin- $\frac{1}{2}$  particles in a magnetic field.
- A collection of 1-dimensional harmonic oscillators.

We will look in particular at properties that can be measured in the laboratory, such as the specific heat capacity and its variation with temperature.

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### Example 1: Spin- $\frac{1}{2}$ solid

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As the first example, we will consider a spin- $\frac{1}{2}$  solid. This consists of a large number of particles (atoms), each of which has a fixed position in space. Each particle has a magnetic moment that can be aligned either parallel or anti-parallel with an external magnetic field.

We shall assume that the magnetic moment of one particle interacts only weakly with those around it. This means that the energy states of each particle are essentially those of an isolated particle; but that particles can exchange energy, so as to achieve an equilibrium distribution of energies.

### Example 1: Spin- $\frac{1}{2}$ solid

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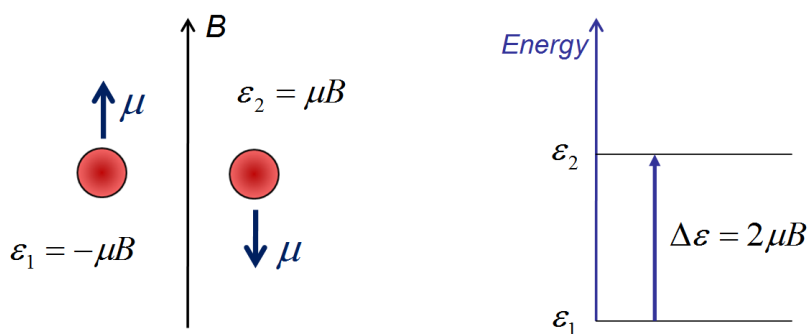
Let us denote the energy levels:

$\varepsilon_1$  : spin parallel to external field;

$\varepsilon_2$  : spin anti-parallel to external field.

We also define the energy difference  $\Delta\varepsilon$  between the energy levels:

$$\Delta\varepsilon = \varepsilon_2 - \varepsilon_1. \quad (4)$$



### Example 1: Spin- $\frac{1}{2}$ solid - populations

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Let us begin by finding the populations of each energy level at a given temperature,  $T$ . The partition function  $Z$  is given by:

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}} = e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}}. \quad (5)$$

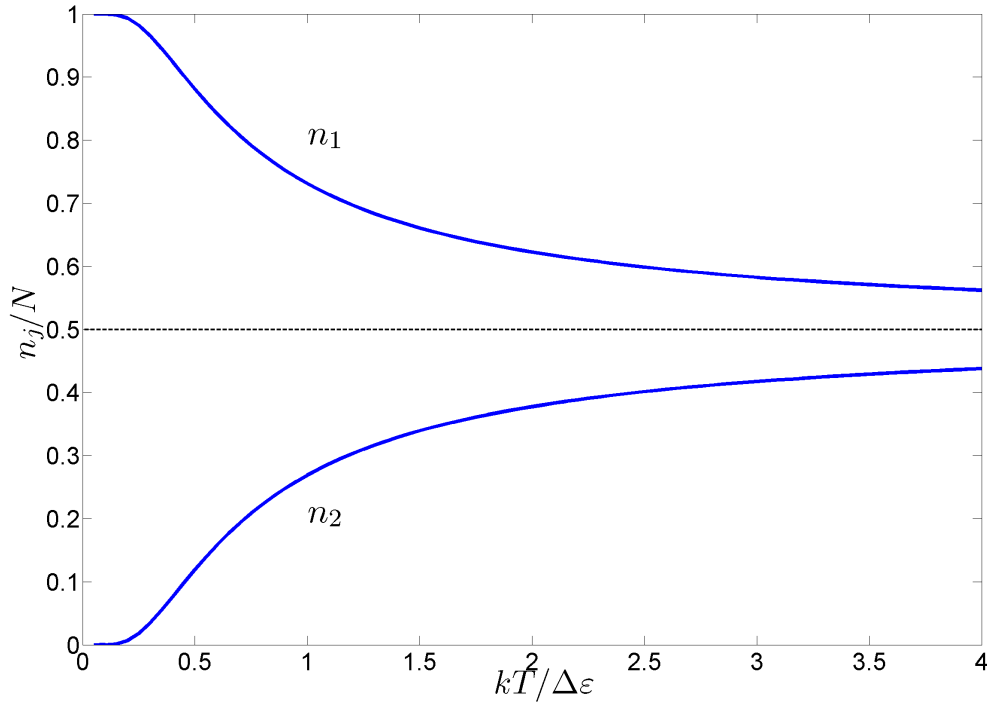
Hence, from the Boltzmann distribution (1), the populations  $n_1$  and  $n_2$  of energy levels  $\varepsilon_1$  and  $\varepsilon_2$  are:

$$n_1 = \frac{N e^{-\frac{\varepsilon_1}{kT}}}{e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}}} = \frac{N}{1 + e^{-\frac{\Delta\varepsilon}{kT}}} \quad (6)$$

and:

$$n_2 = \frac{N e^{-\frac{\varepsilon_2}{kT}}}{e^{-\frac{\varepsilon_1}{kT}} + e^{-\frac{\varepsilon_2}{kT}}} = \frac{N e^{-\frac{\Delta\varepsilon}{kT}}}{1 + e^{-\frac{\Delta\varepsilon}{kT}}} \quad (7)$$

Note that  $n_1 + n_2 = N$ , the total number of particles in the system.



It is worth noting the populations in the limit of low and high temperature. The populations are given by:

$$n_1 = \frac{N}{1 + e^{-\frac{\Delta\varepsilon}{kT}}}, \quad n_2 = \frac{Ne^{-\frac{\Delta\varepsilon}{kT}}}{1 + e^{-\frac{\Delta\varepsilon}{kT}}}. \quad (8)$$

We see that in the low-temperature limit,  $T \rightarrow 0$ :

$$n_1 \rightarrow N, \quad n_2 \rightarrow 0. \quad (9)$$

In other words, all the particles occupy the lowest energy level.

In the high-temperature limit,  $T \rightarrow \infty$ :

$$n_1 \rightarrow \frac{N}{2}, \quad n_2 \rightarrow \frac{N}{2}. \quad (10)$$

In other words, half the particles occupy the lowest energy level, and half occupy the highest energy level.

Now let us consider how the total energy of the system varies with temperature. The total energy  $U$  is given by:

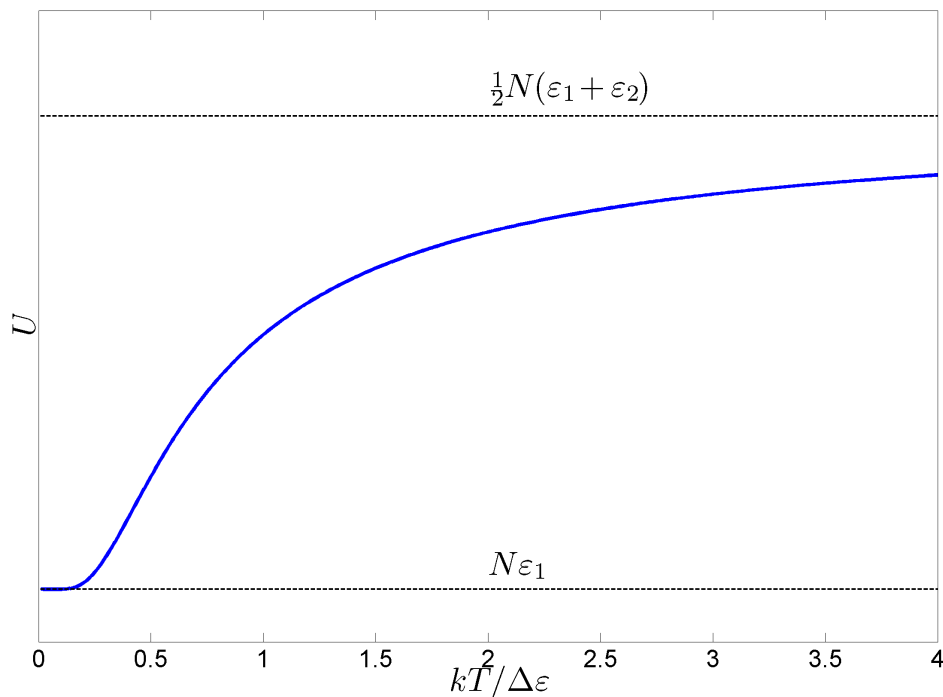
$$U = \sum_j n_j \varepsilon_j = \frac{N \left( \varepsilon_1 + \varepsilon_2 e^{-\frac{\Delta\varepsilon}{kT}} \right)}{1 + e^{-\frac{\Delta\varepsilon}{kT}}} \quad (11)$$

Again, we can find the low-temperature limit:

$$U \rightarrow N\varepsilon_1 \quad \text{as} \quad T \rightarrow 0, \quad (12)$$

and the high-temperature limit:

$$U \rightarrow \frac{1}{2}N(\varepsilon_1 + \varepsilon_2) \quad \text{as} \quad T \rightarrow \infty. \quad (13)$$



The heat capacity at constant volume  $C_V$  is defined by:

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \quad (14)$$

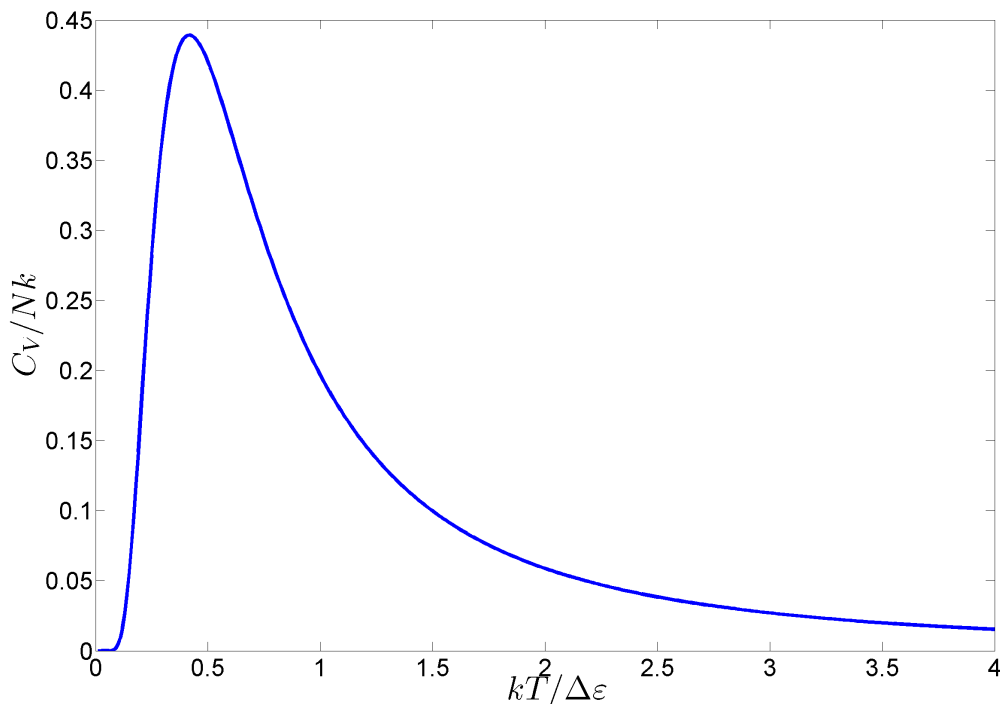
Note that in many systems, the energy levels depend on the volume of the system, so it is necessary to impose the condition of constant volume. This is not the case for the present system of spin- $\frac{1}{2}$  particles in a magnetic field; nonetheless, we shall assume that the volume of the system remains constant.

To find the heat capacity, we use the expression for the total energy (11):

$$U = \frac{N \left( \varepsilon_1 + \varepsilon_2 e^{-\frac{\Delta\varepsilon}{kT}} \right)}{1 + e^{-\frac{\Delta\varepsilon}{kT}}} \quad (15)$$

and take the derivative with respect to  $T$ :

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = N \frac{\Delta\varepsilon^2}{kT^2} \frac{e^{-\frac{\Delta\varepsilon}{kT}}}{\left( 1 + e^{-\frac{\Delta\varepsilon}{kT}} \right)^2} \quad (16)$$



Again, we can take the limits of high and low temperature. The high temperature case is straightforward, and we find:

$$C_V = N \frac{\Delta\varepsilon^2}{kT^2} \frac{e^{-\frac{\Delta\varepsilon}{kT}}}{\left(1 + e^{-\frac{\Delta\varepsilon}{kT}}\right)^2} \rightarrow \frac{N\Delta\varepsilon^2}{4kT^2} \quad \text{as} \quad T \rightarrow \infty. \quad (17)$$

To find the low temperature limit, we define  $x = \Delta\varepsilon/kT$ , in terms of which we write:

$$C_V = Nk \frac{x^2 e^{-x}}{(1 + e^{-x})^2}. \quad (18)$$

Since  $x^2/e^x \rightarrow 0$  as  $x \rightarrow \infty$  ( $T \rightarrow 0$ ), we find that:

$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0. \quad (19)$$

Next let us look at how the entropy of the system changes with temperature. Here, we make use of the Helmholtz free energy:

$$F = U - TS, \quad (20)$$

to write:

$$dF = dU - T dS - S dT. \quad (21)$$

From the first law of thermodynamics:

$$dU = T dS - p dV, \quad (22)$$

so:

$$dF = -p dV - S dT. \quad (23)$$

Hence, we find that:

$$S = - \left( \frac{\partial F}{\partial T} \right)_V. \quad (24)$$

Now we use the relation between the Helmholtz free energy and the partition function:

$$F = -NkT \ln Z. \quad (25)$$

Using equation (5) for the partition function, we find:

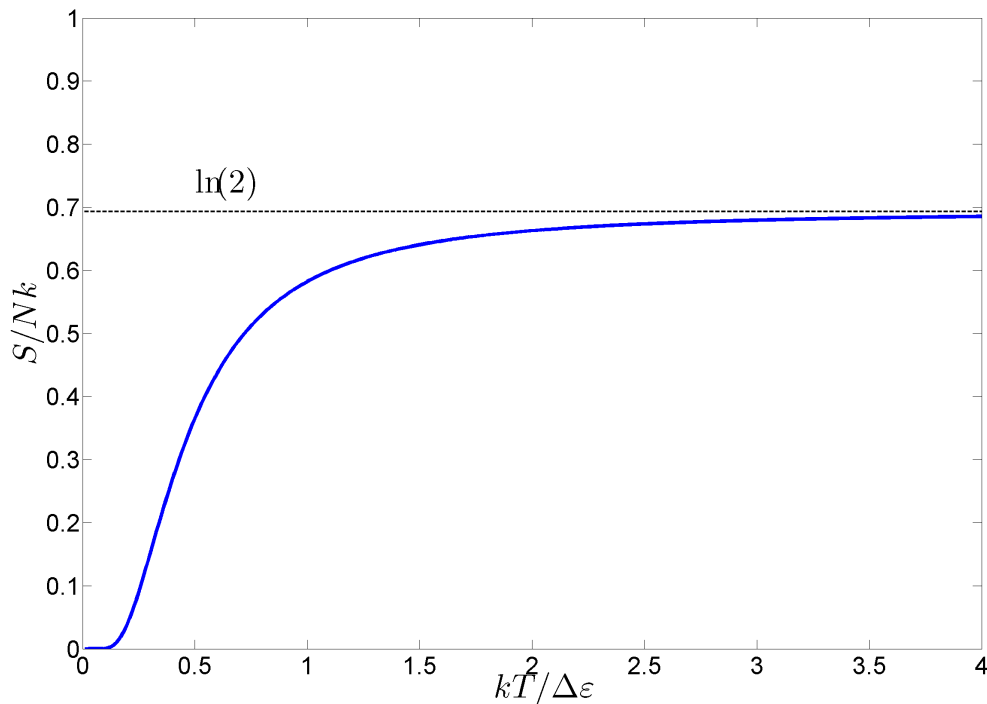
$$F = -NkT \ln \left[ e^{-\frac{\varepsilon_1}{kT}} \left( 1 + e^{-\frac{\Delta\varepsilon}{kT}} \right) \right], \quad (26)$$

$$= -NkT \left[ -\frac{\varepsilon_1}{kT} + \ln \left( 1 + e^{-\frac{\Delta\varepsilon}{kT}} \right) \right], \quad (27)$$

$$= N\varepsilon_1 - NkT \ln \left( 1 + e^{-\frac{\Delta\varepsilon}{kT}} \right). \quad (28)$$

Taking the derivative with respect to temperature  $T$ , we find:

$$S = - \left( \frac{\partial F}{\partial T} \right)_V = Nk \ln \left( 1 + e^{-\frac{\Delta\varepsilon}{kT}} \right) + Nk \frac{(\varepsilon/kT) e^{-\frac{\Delta\varepsilon}{kT}}}{\left( 1 + e^{-\frac{\Delta\varepsilon}{kT}} \right)}. \quad (29)$$





As usual, we look for the low-temperature and the high-temperature limits. We find that:

$$S \rightarrow 0 \quad \text{as} \quad T \rightarrow 0. \quad (30)$$

This is consistent with Boltzmann's equation, since at zero temperature, all particles are in the lowest energy state, and there is only one microstate accessible to the system, i.e.  $\Omega = 1$ . Hence, from Boltzmann's equation:

$$S = k \ln \Omega, \quad (31)$$

we find  $S = 0$ .

In the high temperature limit, we find from equation (29):

$$S = Nk \ln \left( 1 + e^{-\frac{\Delta \varepsilon}{kT}} \right) + Nk \frac{(\varepsilon/kT) e^{-\frac{\Delta \varepsilon}{kT}}}{\left( 1 + e^{-\frac{\Delta \varepsilon}{kT}} \right)}. \quad (32)$$

that:

$$S \rightarrow Nk \ln 2 \quad \text{as} \quad T \rightarrow \infty. \quad (33)$$

This is also consistent with Boltzmann's equation. At very high temperature, half the particles are in the lower energy state, and half are in the higher energy state. Since each of the  $N$  particles can be in one of two states with equal probability, the number of microstates accessible to the system is  $\Omega = 2^N$ .

Hence:

$$S = k \ln \Omega = k \ln 2^N = Nk \ln 2. \quad (34)$$

Finally, we consider the magnetisation of the system. The magnetisation  $M$  is defined as the magnetic moment induced in the solid by an external field  $B$ . Since  $n_1$  particles are in the low energy state, with spin parallel to  $B$ , and  $n_2$  are in the high energy state with spin antiparallel to  $B$ , the magnetisation of the system is:

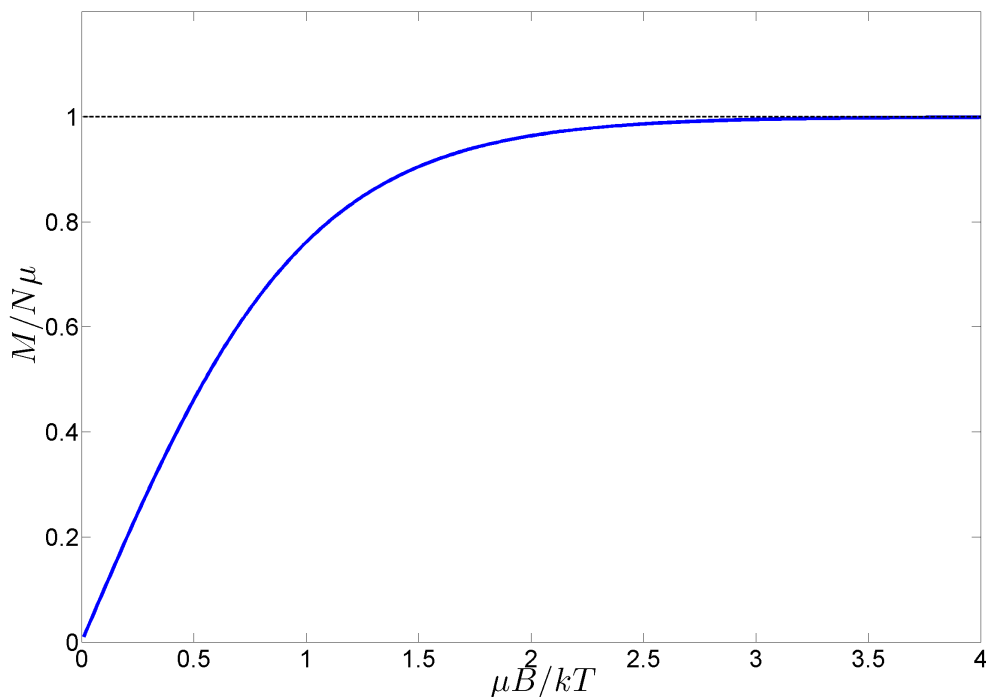
$$M = n_1\mu - n_2\mu. \quad (35)$$

Using the population equations (6) and (6) with  $\varepsilon_1 = -\mu B$  and  $\varepsilon_2 = +\mu B$  leads to:

$$M = N\mu \frac{\left(e^{\frac{\mu B}{kT}} - e^{-\frac{\mu B}{kT}}\right)}{\left(e^{\frac{\mu B}{kT}} + e^{-\frac{\mu B}{kT}}\right)}, \quad (36)$$

which can be written as:

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right). \quad (37)$$



Note the horizontal axis is  $\mu B/kT$ : *inversely* proportional to  $T$ !

At low temperatures,  $kT \ll \mu B$ , we have:

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right) \approx N\mu. \quad (38)$$

Nearly all particles are in the lower energy state, parallel to the magnetic field, and the magnetisation is “saturated”. In this condition, the magnetisation becomes independent of field strength and temperature.

At high temperatures,  $kT \gg \mu B$ , then:

$$M \approx N \frac{\mu^2 B}{kT}. \quad (39)$$

In this state, the magnetisation varies in proportion to the field strength, and in inverse proportion to the temperature.

Equation (39) expresses Curie’s law for a spin- $\frac{1}{2}$  paramagnetic material. The theory for solids having higher spin is similar, but more complicated.

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### Example 2: $N$ localised one-dimensional harmonic oscillators

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We briefly discussed the quantum harmonic oscillator when introducing the principles of statistical mechanics in Part 1 of this course. We shall now consider a collection of a large number  $N$  of quantum harmonic oscillators. We shall aim to calculate the energy, heat capacity and entropy of this system as functions of temperature.

Although this system may at first appear artificial, it may be used as a very simple model of a solid, in which the particles are able to oscillate about fixed positions. If there are  $N$  particles in the solid, each able to oscillate in three dimensions, then the solid may be treated as a collection of  $3N$  one-dimensional oscillators.

We shall first derive some results, then discuss the successes and failures of this system as a model for a solid.

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### Example 2: $N$ localised one-dimensional harmonic oscillators

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Recall (from courses on quantum mechanics) that the allowed energy levels in a quantum harmonic oscillator are given by:

$$\varepsilon_j = \left(\frac{1}{2} + j\right)\hbar\omega, \quad (40)$$

where  $j = 0, 1, 2, 3, \dots$  is zero or a positive integer, and  $\omega$  is the characteristic frequency of the system (which is related to the mass of the particle and the potential energy).  $\hbar$  is Planck's constant divided by  $2\pi$ .

We shall consider a (large) number  $N$  of such oscillators. As usual, we shall assume that the interactions between the oscillators are weak, so they can exchange energy and reach an equilibrium distribution, but have essentially the same energy levels as isolated oscillators.

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### Example 2: $N$ localised one-dimensional harmonic oscillators

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We shall aim to calculate the total energy of the system, the heat capacity, and the entropy as functions of temperature.

We begin with the total energy,  $U$ . There are two ways to calculate  $U$ . We can either sum the energy levels weighted by the populations (given by the Boltzmann distribution):

$$U = \sum_j n_j \varepsilon_j, \quad n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}. \quad (41)$$

Or, we can use the relation:

$$U = N \frac{d \ln(Z)}{d\beta}, \quad \beta = -\frac{1}{kT}. \quad (42)$$

Either way, we need the partition function,  $Z$ :

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}}. \quad (43)$$

Let's calculate the total energy  $U$  using both methods, and compare the results.

First, we need to evaluate the partition function,  $Z$ :

$$Z = \sum_j e^{-\frac{\varepsilon_j}{kT}} = \sum_j \exp\left(-\left(\frac{1}{2} + j\right) \frac{\theta}{T}\right), \quad (44)$$

where we have defined the parameter  $\theta$  (with units of temperature) such that:

$$k\theta = \hbar\omega. \quad (45)$$

The right hand side is a geometric progression, which we can evaluate:

$$Z = \frac{e^{-\frac{\theta}{2T}}}{1 - e^{-\frac{\theta}{T}}}. \quad (46)$$

Now we use the expression for the energy  $\varepsilon_j = (\frac{1}{2} + j)\hbar\omega$  in equation (41) for the total energy  $U$ , to find:

$$U = \frac{N}{Z} \sum_j \left(\frac{1}{2} + j\right) k\theta \exp\left(-\left(\frac{1}{2} + j\right) \frac{\theta}{T}\right). \quad (47)$$

The right hand side can be expressed as the sum of two geometric progressions. We find:

$$U = \frac{N}{Z} k\theta e^{-\frac{\theta}{2T}} \left[ \frac{1}{2\left(1 - e^{-\frac{\theta}{T}}\right)} + \frac{e^{-\frac{\theta}{T}}}{\left(1 - e^{-\frac{\theta}{T}}\right)^2} \right]. \quad (48)$$

Finally, substituting in expression (46) for the partition function  $Z$ , we obtain:

$$U = Nk\theta \left[ \frac{1}{2} + \frac{1}{\left(e^{\frac{\theta}{T}} - 1\right)} \right]. \quad (49)$$

We can check this result by using the second of the two formulae for the total energy,  $U$ , equation (42):

$$U = N \frac{d \ln(Z)}{d\beta}, \quad \beta = -\frac{1}{kT}.$$

We write the partition function (46) in the form:

$$Z = \frac{e^{\frac{1}{2}k\theta\beta}}{1 - e^{k\theta\beta}}, \quad (50)$$

and take the logarithm:

$$\ln(Z) = \frac{1}{2}k\theta\beta - \ln(1 - e^{k\theta\beta}). \quad (51)$$

Taking the derivative with respect to  $\beta$ :

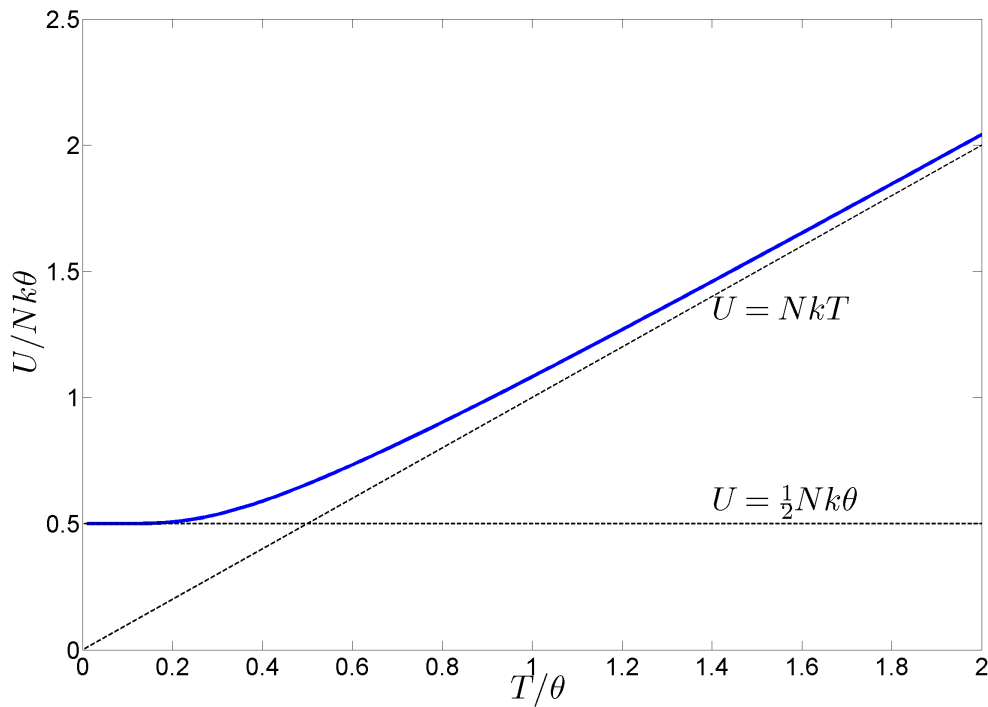
$$\frac{d \ln(Z)}{d\beta} = \frac{1}{2}k\theta + \frac{k\theta e^{k\theta\beta}}{(1 - e^{k\theta\beta})} \quad (52)$$

$$= \frac{1}{2}k\theta + \frac{k\theta}{(e^{-k\theta\beta} - 1)}. \quad (53)$$

So we find, having started from equation (42):

$$U = Nk\theta \left[ \frac{1}{2} + \frac{1}{(e^{\frac{\theta}{T}} - 1)} \right].$$

This is in agreement with the expression we found for the total energy  $U$  (49), starting from (41).



Let us look at the low temperature and high temperature limits of the total energy (49):

$$U = Nk\theta \left[ \frac{1}{2} + \frac{1}{\left(e^{\frac{\theta}{T}} - 1\right)} \right].$$

We see that:

$$U \rightarrow \frac{1}{2}Nk\theta \quad \text{as} \quad T \rightarrow 0 \quad (T \ll \theta), \quad (54)$$

and:

$$U \rightarrow NkT \quad \text{as} \quad T \rightarrow \infty \quad (T \gg \theta). \quad (55)$$

Now we proceed to find the heat capacity,  $C_V$ . Recall that this is simply the derivative of the total energy  $U$  with respect to temperature  $T$ , at constant volume  $V$ :

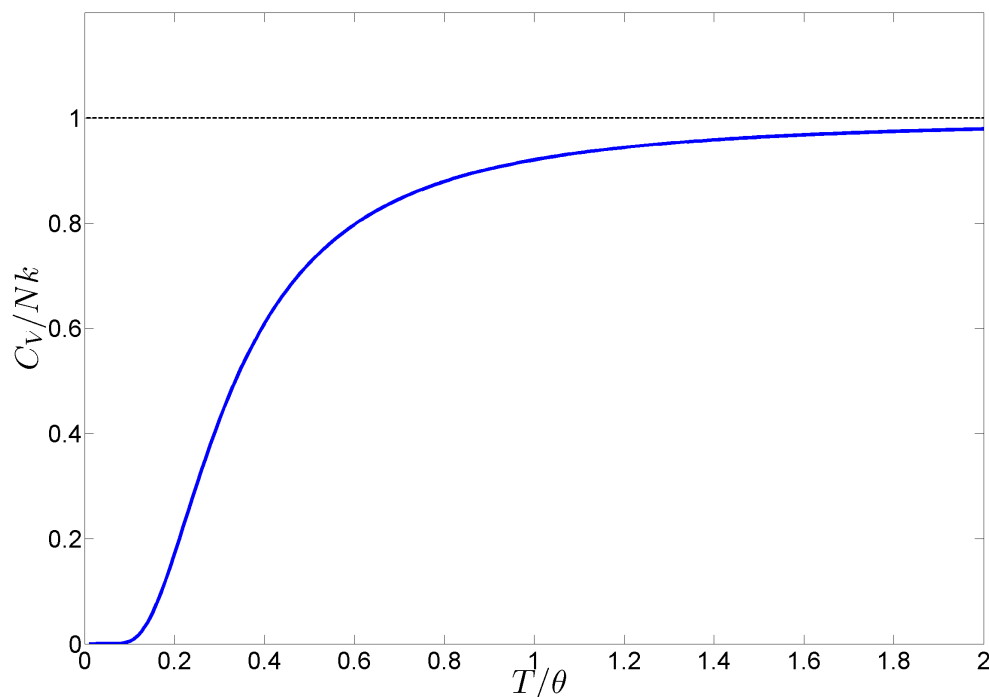
$$C_V = \left( \frac{\partial U}{\partial T} \right)_V. \quad (56)$$

Using equation (49) for the energy:

$$U = Nk\theta \left[ \frac{1}{2} + \frac{1}{\left( e^{\frac{\theta}{T}} - 1 \right)} \right],$$

we find:

$$C_V = Nk \frac{\left( \frac{\theta}{T} \right)^2 e^{\frac{\theta}{T}}}{\left( e^{\frac{\theta}{T}} - 1 \right)^2}. \quad (57)$$





As usual, we look at the low temperature and high temperature limits. From equation (57):

$$C_V = Nk \frac{\left(\frac{\theta}{T}\right)^2 e^{\frac{\theta}{T}}}{\left(e^{\frac{\theta}{T}} - 1\right)^2}.$$

We see that:

$$C_V \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 \quad (T \ll \theta), \quad (58)$$

and:

$$C_V \rightarrow Nk \quad \text{as} \quad T \rightarrow \infty \quad (T \gg \theta). \quad (59)$$

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$N$  harmonic oscillators: entropy

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Finally, we look at the entropy. As in the case of the spin- $\frac{1}{2}$  solid, we obtain the entropy from the expression for the Helmholtz free energy,  $F$ :

$$S = - \left( \frac{\partial F}{\partial T} \right)_V. \quad (60)$$

We use:

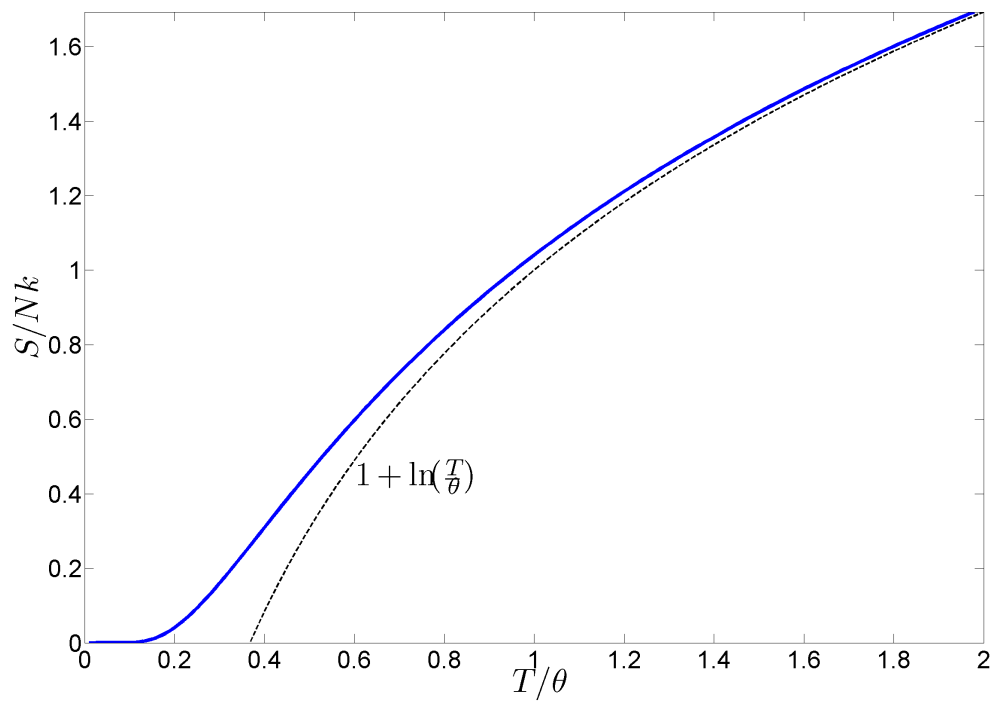
$$F = -NkT \ln(Z), \quad (61)$$

and the expression (46) for the partition function:

$$Z = \frac{e^{-\frac{\theta}{2T}}}{1 - e^{-\frac{\theta}{T}}}.$$

Following the same procedure as for the spin- $\frac{1}{2}$  solid, we find:

$$S = Nk \left[ \frac{\theta/T}{\left(e^{\frac{\theta}{T}} - 1\right)} - \ln \left( 1 - e^{-\frac{\theta}{T}} \right) \right]. \quad (62)$$



From expression (62) for the entropy:

$$S = Nk \left[ \frac{\theta/T}{\left(e^{\theta/T} - 1\right)} - \ln \left(1 - e^{-\theta/T}\right) \right], \quad (63)$$

we can derive the low temperature limit:

$$S \rightarrow 0 \quad \text{as} \quad T \rightarrow 0 \quad (T \ll \theta), \quad (64)$$

and the high temperature limit:

$$S \rightarrow Nk \left[ 1 + \ln \left( \frac{T}{\theta} \right) \right] \quad \text{as} \quad T \rightarrow \infty \quad (T \gg \theta). \quad (65)$$

The range of temperatures for which  $T \approx \theta$ , may be regarded as dividing the quantum regime ( $T \ll \theta$ ) from the classical regime ( $T \gg \theta$ ).

At high temperatures, the average energy per oscillator is  $kT$ , and this is much larger than the gap between energy levels: the range of allowed energies may be regarded as essentially continuous.

At low temperatures,  $kT$  becomes close to  $k\theta (= \hbar\omega)$ : when this happens, we can no longer ignore the fact that the allowed energies for an oscillator occur at discrete intervals.

In the quantum limit,  $T \rightarrow 0$ , the energy, heat capacity and entropy behave as follows:

$$U \rightarrow \frac{1}{2}Nk\theta, \quad (66)$$

$$C_V \rightarrow 0, \quad (67)$$

$$S \rightarrow 0. \quad (68)$$

There is a “zero-point” energy of  $\frac{1}{2}k\theta (= \frac{1}{2}\hbar\omega)$  per oscillator. The heat capacity and the entropy tend towards zero, as all the oscillators start to fall into the lowest possible energy state. This agrees with what we find for a real solid.

In the classical limit,  $T \rightarrow \infty$ , the energy, heat capacity and entropy behave as follows:

$$U \rightarrow NkT, \quad (69)$$

$$C_V \rightarrow Nk, \quad (70)$$

$$S \rightarrow Nk \left[ 1 + \ln \left( \frac{T}{\theta} \right) \right]. \quad (71)$$

The energy and heat capacity behave as expected for a real solid (except that we have to replace  $N$  by  $3N$ , to account for motion in three dimensions).

The entropy is interesting: we notice that Planck's constant still appears, even in the classical limit. It seems that entropy is intrinsically a quantum effect.

We should emphasise that the behaviour of the entropy in the classical limit that we find in this system does agree with the classical theory. According to the first law of (classical) thermodynamics:

$$dU = T dS - p dV. \quad (72)$$

At constant volume:

$$dU = T dS. \quad (73)$$

In the classical theory,  $C_V = Nk$  is a constant, so we can write:

$$U = C_V T \quad \therefore \quad dU = Nk dT. \quad (74)$$

Hence:

$$\int_{S_0}^S dS = Nk \int_{T_0}^T \frac{dT}{T}, \quad (75)$$

and so:

$$S = S_0 + Nk \ln \left( \frac{T}{T_0} \right). \quad (76)$$

Compare the expression for the entropy from classical thermodynamics, equation (76):

$$S = S_0 + Nk \ln \left( \frac{T}{T_0} \right)$$

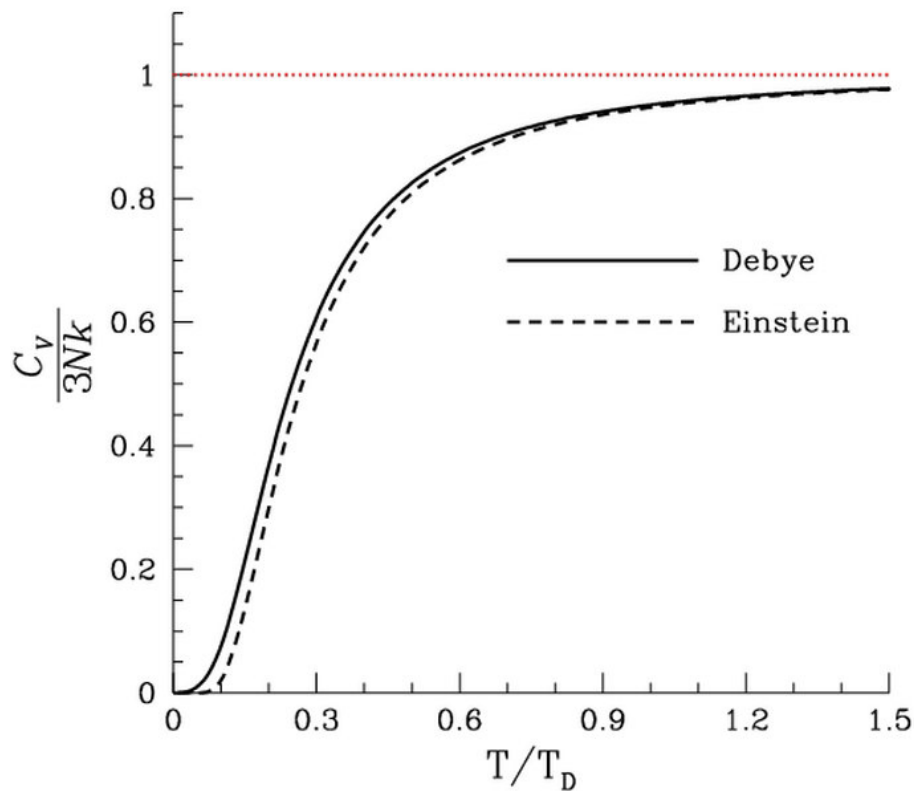
with the expression from statistical mechanics (71), derived using a model of  $N$  quantum harmonic oscillators:

$$S \rightarrow Nk + Nk \ln \left( \frac{T}{\theta} \right) \quad \text{as} \quad T \rightarrow \infty.$$

In classical thermodynamics, there is no way to derive the values of the constants  $S_0$  and  $T_0$ : put another way, it is impossible to find the value of the entropy of a system at absolute zero. Using statistical mechanics and quantum mechanics, there are no uncertainties: we have an expression involving known constants and quantities, that corresponds to the classical model in the high temperature regime.

The model of a solid that we have developed is known as the Einstein model. It gives the correct behaviour in the low temperature and high temperature limits. But in the intermediate regime, it fails to describe accurately the properties of real solids.

The Debye model, in which the vibrational energy of the atoms is treated as a gas of “phonons”, gives a more accurate description of the behaviour of solids at low temperatures.



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## Summary

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You should be able to:

- Explain how the partition function is calculated in a statistical system.
- Explain how the partition function can be used to calculate the energy and entropy of a system as functions of temperature.
- Calculate the populations; total energy; heat capacity; entropy; and magnetisation of a spin- $\frac{1}{2}$  solid, all as functions of temperature.
- Calculate, as functions of temperature, the total energy; heat capacity; and entropy of a system consisting of many 1-dimensional quantum harmonic oscillators.